

Units of Gas Permeability Constants

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Synopsis

Gas permeability constants of polymers are generally expressed by composite units which contain

$$\frac{(\text{amount of gas})(\text{thickness of membrane})}{(\text{membrane area})(\text{time})(\text{differential pressure of gas})}$$

Numerous combinations of various units to express each component unit are used. However, permeability constants of nongaseous substances in polymer membranes are generally expressed by the units of cm^2/sec , which are identical to the units of the diffusion constant. The relationship between constants in units of cm^2/sec and conventional composite units for gas permeability constants is presented, and the advantage of using the units in cm^2/sec to express gas permeability constants is discussed.

INTRODUCTION

In a recently published paper dealing with the gas permeability of microporous polymer membranes,¹ the details of the difference between gas permeability constants in conventional composite units of $\text{cm}^3(\text{S.T.P.})\text{-cm}/\text{cm}^2\text{-sec-cm Hg}$ and the permeability constants of microporous membranes, which turned out to be given by cm^2/sec , was intended to be presented in an appendix at the end of the paper. However, the appendix was inadvertently left out, and no details are presented in the paper. Since many questions concerning this point have arisen, it seems appropriate to present a more detailed discussion of the units of gas permeability constants than was presented in the previous paper.

Permeability constants of polymer membrane to nongaseous permeants are generally expressed by the units which have dimensions of L^2/T (e.g., cm^2/sec). Therefore, presenting gas permeability constants by composite units such as $\text{cm}^3(\text{S.T.P.})\text{-cm}/\text{cm}^2\text{-sec-cm Hg}$ is rather unconventional in view of the general expression by which permeability constants of membranes to various permeants are described.

The comparison of gas permeability constants in different units, then, may be best accomplished by comparing the units of permeability constants of various permeants (e.g., solutes, dissolved gases, and gases).

It should be noted that the permeability constant P of a membrane to a permeant is an empirical expression of the ease of transport of the permeant through the membrane and can be generally defined by the relationship

$$J/A = P(\text{driving force gradient})$$

where J is the flux of the permeant (e.g., moles/sec) and A is the membrane area. The driving-force gradient, in terms of practical measurement, is the differential driving force measured in both sides (external phases) of a membrane, divided by the membrane thickness (e.g., $\Delta C/l$ and $\Delta p/l$, where ΔC is the differential concentration, Δp is the differential partial pressure, and l is the thickness of the membrane).

It should be further recognized that the permeability constant thus defined per se has no relation to the mechanism of transport (e.g., diffusive transport or flux due to the flow mechanism). The permeability constant P of certain polymers to certain permeants in appropriate conditions can be given as the product of the diffusion constant D and the solubility coefficient s (or partition coefficient), i.e., $P = Ds$. However, the measurement of flux alone does not lead to this relationship, and this relationship should not be assumed as a part of the definition of the permeability constant. Gas permeability constants of microporous membranes provide good examples to illustrate this point.

The inherent empirical nature of the permeability constant stems from the ambiguity of the driving force taken in the measurement and its relationship to the true driving force of the transport, which cannot be determined without additional experiments to confirm it.

In this paper, the discussion is limited to the units used to express gas permeability constants. Therefore, the permeability constant is dealt with in the empirical context, and there is no need to elucidate the transport mechanism for this purpose.

UNITS OF PERMEABILITY CONSTANTS OF NONGASEOUS PERMEANTS

Permeability Constants of Solutes

First, let us consider the simple case of the permeability of urea (dissolved in water) in a polymer membrane. In this case, the concentration gradient is created across the membrane and the flux of urea is measured. The steady-state flux J/A at a constant concentration gradient $\Delta C/l$ (where l is the thickness of the membrane) is related to the permeability coefficient P of the polymer membrane to urea as follows:

$$J/A = P \frac{\Delta C}{l}. \quad (1)$$

where A is the area of the membrane and J is the mass flux per unit time.

In this process of calculating the permeability coefficient P , the flux and the concentration are expressed in terms of identical units. For instance, if moles are used to express the flux (moles/cm²-sec), the concentration is expressed also by moles (e.g., $\Delta C = \text{moles/cm}^3$). Units involved in both sides of eq. (1) are

$$\begin{aligned} \frac{\text{moles}}{\text{cm}^2\text{-sec}} &= P \cdot \frac{\text{moles/cm}^3}{\text{cm}} \\ &= P \cdot \frac{\text{moles}}{\text{cm}^4}. \end{aligned} \quad (1a)$$

Consequently, the unit of P is cm^2/sec , which is identical to the unit of the diffusion constant D . As long as the same unit is used to express the amount of permeant in the flux and in the concentration, the permeability is always given in cm^2/sec , regardless of the units used (e.g., grams, moles, radioactivity counts, etc.).

The permeability coefficient differs from the diffusion coefficient D by a factor of the partition coefficient σ (dimensionless number); i.e.,

$$P = \sigma D \quad (2)$$

The partition coefficient σ is given by the ratio of concentration in solution to the concentration in the membrane phase at the equilibrium state:

$$\begin{aligned} \sigma &= \frac{\text{concentration in membrane}}{\text{concentration in solution}} \\ &= \frac{\text{moles/cm}^3 \text{ in membrane}}{\text{moles/cm}^3 \text{ in solution}} \end{aligned} \quad (3)$$

As long as the same units are used to express concentration in solution and in membrane, the partition coefficient is a dimensionless number. This is the units of permeability coefficient widely used to express permeabilities of varieties of solutes in dialysis membranes.

Permeability Constants of Dissolved Gas

Now let us consider another simple case, in which urea is replaced by oxygen, i.e., dissolved oxygen in water (of a certain concentration) on one side of the identical membrane discussed above and dissolved oxygen in water (of a different concentration) on another side. Following the exact same procedure of calculating the permeability of the membrane to urea as that mentioned above, we obtain the oxygen permeability, which is given in units of cm^2/sec . In this hypothetical experiment, we obtained the gas permeability (oxygen permeability) in units of cm^2/sec ; the value can be directly compared with the value of the permeability coefficient of urea in the same membrane.

If the membrane under consideration is a homogeneous (nonporous) polymer membrane, the gas permeability constant obtained by the above procedure should be identical to the gas permeability constant obtained by the gas phase experiment, since the true driving force is the partial pressure difference of the gas, which is independent of the concentration of O_2 in the phases involved (i.e., gas phase or dissolved gas).²

UNITS OF PERMEABILITY CONSTANT OF GASES

A question concerning the unit of the permeability coefficient arises when we measure the oxygen permeability of the same membrane by the conventional gas-phase experiments. In the determination of gas permeabilities by gas-phase experiments, the gas flux is often expressed in $\text{cm}^3(\text{S.T.P.})/\text{cm}^2\text{-sec}$, and the differential pressure Δp is used as the differential driving force; i.e., the flux-driving force gradient relationship similar to eq. (1) is given by

$$J/A = P \frac{\Delta p}{l}. \quad (4)$$

Units involved in both sides of the equation can be written as

$$\frac{\text{cm}^3(\text{S.T.P.})}{\text{cm}^2\text{-sec}} = P' \frac{\text{cmHg}}{\text{cm}} \quad (4a)$$

The choice of units leads to complex composite units, including units of pressure for the gas permeability coefficient. The units of $\text{cm}^3(\text{S.T.P.})\text{-cm}/\text{cm}^2\text{-sec-cm Hg}$ have been widely used in the literature to express the gas permeability coefficient in recent years.

These units have the practical merit of being able to calculate gas flux in different conditions, since the units of practical parameters, such as membrane area, thickness, and applied differential pressure, are included in the composite units. However, these units have a disadvantage in that it is difficult to compare the value of permeability with those for other substances. For instance, permeabilities of urea, NaCl, alcohol, etc., in membranes are all expressed in cm^2/sec , whereas the oxygen permeability obtained by a gas-phase experiment is expressed in $\text{cm}^3(\text{S.T.P.})\text{-cm}/\text{cm}^2\text{-sec-cm Hg}$.

Within the framework of our theoretical consideration, we are still dealing with the oxygen permeability of the same membrane (disregarding minor variations such as the concentration-polarization effect in the dissolved oxygen experiment and the effect of water on the polymer). Therefore, these two oxygen permeabilities should be identical. The relationship between two permeability constants in different units can be seen as follows.

It should be recognized that in eq. (4a) for the gas permeability constant, the general rule of expressing the amount of permeant in flux and in the driving force by an identical unit is not obeyed, and this is the origin of the more complex composite units for gas permeability constants.

The gas flux is generally measured by either the rate of pressure change at a fixed volume or by the rate of volume change at a fixed pressure, i.e., $V(dp/dt)$ or $p(dV/dt)$, respectively. In more general form, the gas flux is measured by $d(pV)/dt$. In the process of calculating gas flux in $\text{cm}^3(\text{S.T.P.})$, $d(pV)/dt$ is converted to $\text{cm}^3(\text{S.T.P.})$ by the equation

$$\frac{d[\text{cm}^3(\text{S.T.P.})]}{dt} = \frac{d(pV)}{dt} \cdot \frac{T_0}{T} \cdot \frac{1}{(\text{pressure corresponding to 1 atm})} \quad (5)$$

Now, it should be realized that cm^3 is a unit of volume; however, $\text{cm}^3(\text{S.T.P.})$ is not a unit of volume but a unit to express the number of molecules. The term $\text{cm}^3(\text{S.T.P.})$ is essentially in units of $p \times V$, i.e., cm^3 of gas at 1 atm and at 273°K .

If the symbol M is used to express $\text{cm}^3(\text{S.T.P.})$,

$$M \equiv \text{cm}^3(\text{S.T.P.}) \quad (6)$$

$$M = (pV) \frac{1}{\alpha} \frac{T_0}{T}$$

where α is the conversion factor of the pressure unit to 1 atm; e.g., when cm Hg is used, $\alpha = 76$; when mm Hg is used, $\alpha = 760$; when dyne/cm² is used, $\alpha = 1.013 \times 10^6$; and $T_0 = 273^\circ\text{K}$; T is the temperature of the measurement in $^\circ\text{K}$.

From eq. (4) and eq. (6),

$$\frac{1}{A} \frac{d(pV)}{dt} \left(\frac{1}{\alpha} \frac{T_0}{T} \right) = P' \frac{\Delta P}{l}. \quad (7)$$

Following the general rule of using the same unit of pressure in both pV and Δp , the units of P' are given by $(\text{cm}^2/\text{sec})(T_0/\alpha T)$.

Since $(1/\alpha \cdot T_0/T)$ is a dimensionless number, P' is essentially given in units of cm^2/sec , and its numerical value differs from P' expressed by the composite units by a factor of $(T_0/\alpha T)$.

This means that the gas permeability coefficient units of cm^2/sec can be obtained simply by omitting the process of converting the gas flux into $\text{cm}^3(\text{S.T.P.})$. This can be done by expressing the gas flux as

$$J/A = \frac{1}{A} \frac{d(pV)}{dt}$$

and using the same pressure unit in both pV and Δp in eq. (4). Thus,

$$\begin{aligned} P[\text{in cm}^2/\text{sec}] &= P'[\text{in cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{atm}] \times \frac{T}{T_0} \\ &= P'[\text{in cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}] \times \frac{T}{T_0} \times 76. \end{aligned}$$

This relationship can be generally expressed by

$$P = [\text{in cm}^2/\text{sec}] = P'[\text{in cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot (\text{pressure})] \times \frac{T}{T_0} \times \alpha. \quad (8)$$

Since $\text{cm}^3(\text{S.T.P.}) \cdot T/T_0$ is the actual volume of a gas at 1 atm and at the temperature of the measurement, the values of P (in cm^2/sec) provide a gas flux in volume at the temperature of the measurement and at 1 atm, which occurs under the differential pressure of 1 atm through the membrane area of 1 cm^2 .

INTERPRETATION OF GAS PERMEABILITY CONSTANTS IN cm^2/sec FOR HOMOGENEOUS POLYMER FILMS

For a flawless homogeneous polymer film, the gas permeability constant is the product of the diffusion constant and the solubility constant. If the gas permeability constant is given by the composite units of $\text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}$, the units of solubility constant are given by

$$\begin{aligned} s &= \frac{P'}{D} \\ &= \frac{\text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}}{\text{cm}^2/\text{sec}} \\ &= \frac{\text{cm}^3(\text{S.T.P.})}{\text{cm}^3 \cdot \text{cmHg}}. \end{aligned}$$

On the other hand, if the gas permeability constant is expressed in cm^2/sec , the units of the solubility constant are given by

$$\begin{aligned}\sigma &= \frac{P}{D} \\ &= \frac{\text{cm}^2/\text{sec}}{\text{cm}^2/\text{sec}} \\ &= \text{dimensionless number.}\end{aligned}$$

In this case, σ is more adequately represented by the partition coefficient, which is a dimensionless number.

The relationship between s and σ can be obtained by virtue of eq. (8) as

$$\sigma = s \left(\frac{T}{T_0} \right) \alpha. \quad (9)$$

In such a partition coefficient for gas phase and solid phase, it may appear difficult to find the physical meaning at first glance; however, the close examination of Henry's law constant reveals that σ is essentially a Henry's law constant.

The Henry's law constant is the amount of gas in a unit volume of a condensed phase (liquid or solid) at the equilibrium with 1 atm of the pure gas. If the same unit is used to express the amount of gas molecules in unit volume of both phases, the Henry's law constant is essentially a partition coefficient between two phases. For instance,

$$\frac{(\text{moles of gas})/\text{cm}^3 \text{ of condensed phase}}{(\text{moles of gas})/\text{cm}^3 \text{ of gas phase at 1 atm}}$$

leads to a dimensionless coefficient.

Henry's law constant is often expressed by $\text{cm}^3(\text{S.T.P.})$ of gas in liquid or solid equilibrated with 1 atm of pure gas. If this value is expressed by

$$\bar{a} \left(\text{i.e., } \bar{a} = \frac{\text{cm}^3(\text{S.T.P.}) \text{ of gas}}{\text{cm}^3 \text{ polymer at 1 atm}} \right),$$

Henry's law constant \bar{a} is given by

$$\bar{a} = \sigma \times \frac{T_0}{T}.$$

It should be noted that the conversion factor in eqs. (8) and (9) (i.e., T/T_0) is due to the definition of the standard state being 1 atm and 273°K , and that if units other than $\text{cm}^3(\text{S.T.P.})$ are used to express gas flux, this factor disappears and the permeability constant of gas is given in cm^2/sec as long as the same unit is used in the driving force gradient.

It should be further recognized that the selection of $\text{cm}^3(\text{S.T.P.})$ as the unit to express the amount of gas rather than, for instance, grams of gas, is truly arbitrary. Consequently, there is no reason to consider that the use of $\text{cm}^3(\text{S.T.P.})$ for the amount of gas and $\text{cm}^3(\text{S.T.P.}) \text{ cm}/\text{cm}^2\text{-sec-cm Hg}$ for the gas permeability is preferred over numerous other composite units. Contrary

to this, the permeability units given by cm^2/sec are the most logical units based on the C.G.S. unit system, and therefore should be considered as the fundamental units of the gas permeability coefficient.

The permeability coefficient expressed in units of cm^2/sec has several advantages:

1. The numerical value can be directly compared with permeability coefficients of other (nongaseous) permeants in the same membrane.

2. The solubility coefficient is the partition coefficient, which may provide a numerical expression of the significance of the membrane phase for transport of gas.

3. The numerical value itself, without any further conversion, can be used to detect the deviation of the transport mechanism from the diffusive-type permeation. For instance, the diffusion constants of small molecules in condensed phases (liquid and solid) are generally on the order of $10^{-5} \text{ cm}^2/\text{sec}$ and less at near-room temperature. The permeability coefficient in polymers in which the partition coefficient is less than unity (most permanent gases) must be smaller than this limit of $10^{-5} \text{ cm}^2/\text{sec}$. Therefore, this will set the upper limit of P for the diffusive transport. An apparently high permeability constant of a membrane obtained by gas phase experiment may be due to porous structure, but the values of the permeability constant itself cannot show the difference due to diffusive transport and flow through porous structure. If the permeability constant exceeds the order of $10^{-5} \text{ cm}^2/\text{sec}$, however, it certainly indicates that the transport is not diffusive. This kind of judgment, based on the limit, cannot be made with the value of the constant expressed in $\text{cm}^3(\text{S.T.P.})\text{-cm}/\text{cm}^2\text{-sec-cm Hg}$ alone.

4. Regardless of the mode of experiment—such as gas/gas, gas/dissolved gas, dissolved gas/dissolved gas, and dissolved gas/gas—the expression of permeability in units of cm^2/sec may have an advantage over the use of other composite units when dealing with those permeations of gas through membranes that occur in several phases. The practical advantage of the other composite units, P' (experimental parameters are included in P'), only exists in gas-phase experiments.

CONCLUSIONS

1. Gas permeability can be expressed by the universal unit for permeability of cm^2/sec .

2. Calculation of P (in cm^2/sec) from data obtained by gas-phase experiment is actually simpler than the calculation of P' in $\text{cm}^3(\text{S.T.P.})\text{-cm}/\text{cm}^2\text{-sec-cm Hg}$, since the conversion of gas volume to $\text{cm}^3(\text{S.T.P.})$ is not necessary. The gas flux measured either in terms of pressure change or of volume change is related to the differential partial pressure of the gas as

$$\frac{1}{A} \frac{d(pV)}{dt} = P \frac{\Delta p}{l}$$

where A is the membrane area, Δp is the differential pressure, l is the thickness of membrane, and P is the gas permeability of the membrane; P in cm^2/sec is obtained by using the same unit of pressure in $d(pV)$ and Δp , cm for l ,

cm² for A , cm³ for V , and seconds for time t . The direct reading of a pressure gauge, e.g., in mV, can be used in this calculation without converting to such pressure as cm Hg, as long as the same gauge is used in the measurements in $d(pV)$ and in Δp , and providing that the readout is linear with respect to the pressure. Conversely, in the calculation of P' , the pressure must be measured in or converted to units of cm Hg.

3. P and P' , $P/D = \sigma$, and $P'/D = s$ are related as follows:

$$P = P' \left(\frac{T}{T_0} \right) \alpha$$

$$\sigma = s \left(\frac{T}{T_0} \right) \alpha$$

where α is the conversion factor of a pressure unit to 1 atm, T_0 is 273°K, and T is the temperature of the measurements in °K.

4. Henry's law constant \bar{a} is related to σ and s as follows:

$$\bar{a} = \sigma \times \frac{T_0}{T}$$

and

$$\bar{a} = s \times \alpha$$

where \bar{a} is cm³(S.T.P.) of gas in cm³ of condensed phase equilibrated with the pure gas at 1 atm.

5. P has certain advantages over P' . Numerical values can be directly compared with permeabilities of other solutes, including dissolved gas. The deviation of the transport mechanism from the solution-diffusion process can be detected if the numerical values exceed the theoretical upper limit of the diffusive transport.

6. The conversion of values in P to P' is just as simple as the conversion of values of P' in one composite unit to other composite units, if such composite units are needed for some practical purpose.

The author extends his thanks to Dr. V. T. Stannett, Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina, for his valuable discussion on this subject.

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Received December 20, 1974

Revised January 28, 1975